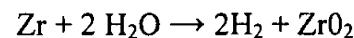


water and/or steam. Zirconium and its alloys are widely used as nuclear fuel cladding since they advantageously possess low neutron absorption cross-sections, and at temperatures below about 398°C (the approximate core temperature of an operating nuclear reactor), are non-reactive and importantly possess high corrosion resistance relative to other metal alloys in the presence of de-mineralized water or steam. Two widely used zirconium alloys (Zircaloys) are Zircaloy-2 and Zircaloy-4. Zircaloy-2, a Zr-Sn-Ni-Fe-Cr alloy, is generally comprised (by weight) of approximately 1.2-1.7% tin, 0.13-0.20% iron, 0.06-0.15% chromium and 0.05-0.08% nickel. Zircaloy-4 has essentially no nickel, and about 0.2% iron, but is otherwise substantially similar to Zircaloy-2. Zircaloy-2 has enjoyed widespread use and continues to be used at present in nuclear reactors. Zircaloy-4 was developed as an improvement to Zircaloy-2 to reduce problems with hydriding, which causes Zircaloy-2 to become brittle when cooled to ambient temperatures (ie. when the reactor is shut down) after absorbing hydrogen at higher temperatures.

Please replace the last paragraph beginning on page 1 with the following:

Zirconium alloys are among the best corrosion resistant materials when exposed to steam at reactor operating temperatures (less than 398°C, typically 290°C) in the absence of radiation from nuclear fission reactors. The corrosion rate in the absence of neutron bombardment is very low and the corrosion product is a uniform, black film/layer of  $\text{ZrO}_2$  which forms on the exterior surfaces of Zircaloy that are exposed to high temperature steam (uniform corrosion). The black oxide layer of  $\text{ZrO}_2$  usually contains a small (non-stoichiometric) excess of zirconium, and as such, it contains excess electrons giving it a black or grey color. It is also highly adherent to zirconium or Zircaloy surfaces that are exposed to steam.

Please replace the equation on page 2 with the following:



Please replace the second full paragraph on page 2 with the following:

Because gas permeability is typically limited in nuclear fuel rods, a hydrogen rich atmosphere, with a very low H<sub>2</sub>O partial pressure, is generated inside the cladding, often far from the initial perforation, especially if crack growth is significant. The pressure in the hydrogen rich atmosphere is believed to be approximately 1000 psi, which is the pressure experienced inside the cladding near the perforation. Under these conditions, Zircaloy-2 cladding becomes susceptible to hydrogen embrittlement followed by failure by brittle fracture. It is, therefore, desirable to improve the resistance of Zircaloy-2 cladding to cracking, while retaining its resistance to fast fracture.

Please replace the last paragraph beginning on page 3 with the following:

It is observed that a zirconium alloy having a certain microstructural configuration and increased resistance to creep, has increased resistance to hydrogen gas cracking. In this regard, experimental results suggest that hydrogen gas fracture of the zirconium alloy is controlled by the rate of creep at the crack tip in the zirconium alloy. Accordingly, the applicants have discovered a zirconium alloy of a particular microstructure which has increased resistance to creep, and which results in a zirconium alloy with increased resistance to hydrogen cracking. The applicants propose use of such alloy in nuclear fuel cladding due to such alloy's increased resistance to hydrogen cracking, which is problematic with existing zirconium and zirconium alloy fuel cladding.

Please replace the first full paragraph on page 4 with the following:

Accordingly, in a further aspect, the invention comprises a fuel cladding for use in a nuclear reactor having a microstructure in one or more of the embodiments disclosed above. More particularly, in a broad aspect of such embodiments of the invention, the

invention comprises a fuel cladding for use in a nuclear reactor, for cladding nuclear fuel, comprising:

a tube member; and  
said tube member comprised of a zirconium alloy, said alloy having a coarse grained lath alpha microstructure.

Please replace the first full paragraph on page 6 with the following:

A superior creep resistant zirconium alloy is provided for use in nuclear fuel cladding. The creep resistant zirconium alloy is a coarse grained lath alpha zirconium alloy microstructure. "Coarse grained" refers to the size of the grain boundary, and encompasses grains with a grain size greater than  $0.15\mu\text{m}$ .

Please replace the last paragraph beginning on page 6 with the following:

In one embodiment, the microstructure is a lath or acicular structure and includes a lath (or interlamellar boundary) spacing of 0.5 to  $3.0\mu\text{m}$ . Without wishing to be bound by theory, it is believed that the lath spacing provides significant obstacles to dislocations during high strain creep. The lath spacing in the structure creates an effective grain size much smaller than the apparent conventional grain size.

Please replace the first full paragraph on page 7 with the following:

Referring to Figures 1A and 1B, in one embodiment, an annular layer 12 of the above-described creep resistant zirconium alloy can be provided near the inside diameter 14 of fuel cladding 10, while retaining fast fracture resistant and corrosion resistant Zircaloy-2 on the outer portion 16 of the cladding. An annular layer 12 of such creep resistant zirconium alloy provided between a zirconium barrier layer 18 and the Zircaloy-2 cladding 16 of either conventional barrier fuel cladding or Triclad™ fuel cladding would help prevent hydrogen gas cracking from inside the cladding.

Please replace the last paragraph beginning on page 7 with the following:

After heat treatment, the first intermediate is quenched at a high rate to form a second intermediate. In one embodiment, the cooling rate during this quench is within the range from about 20 to about 200°C/second. A high quench rate promotes small second phase precipitate particle size and high solute retention in the matrix of the creep resistant zirconium alloy. This is needed for resistance to nodular corrosion in a boiling water reactor. If the cooling rate was too slow, large second phase precipitate particles would form. If the cooling rate was too fast, very few second phase precipitates would form, and there would be poor uniform corrosion in a boiling water reactor environment.

Please replace the second full paragraph on page 8 with the following:

After cold working, the third intermediate is annealed at an elevated temperature to effect partial recrystallization. In one embodiment, the annealing is conducted within the temperature range from about 580°C to about 640°C.

Please replace the fourth full paragraph on page 9 with the following:

The effect of temperature on the rate of hydrogen gas cracking was also determined at an initial stress intensity of 32 ksi $\sqrt{\text{in}}$ . Hydrogen cracking in plate A was rapid at both 250°C and 325°C, Figures 2A and 3A. Tests on Plate A that were conducted at 250°C exhibited low cracking rates at the initial stress intensity of 32 ksi $\sqrt{\text{in}}$ , but the rate of crack propagation at the highest stress intensities was very similar for both temperatures.

Please replace the first full paragraph on page 10 with the following:

The stress intensity of the 250°C Plate B sample was increased from 34 ksi $\sqrt{\text{in}}$  to 39 ksi $\sqrt{\text{in}}$  which led to another transient increase in the crack propagation rate to  $1 \times 10^{-4}$  in/s followed by a drop to a steady state rate of  $5 \times 10^{-6}$  in/s. It is believed that the

*AB*  
*Crack*

behavior of Plate B at 34 and 39 ksi $\sqrt{\text{in}}$  was consistent with transient growth of the crack tip plastic zone size under primary creep conditions. Once an equilibrium plastic zone size was achieved, steady state creep rates controlled the rate of crack advance. For this reason, Figure 3B shows the locus of steady state cracking rates in addition to the transient cracking behavior.

Please replace the second full paragraph on page 11 with the following:

*AB*

The difference in behavior between cold-worked and partially recrystallized Plate B may be due to either their difference in creep strength or the lower applied stress intensity of the cold-worked sample. It is believed that both were factors. This result is significant because it indicated that no hydrogen gas fracture occurred at low stress intensities relative to the creep cracking threshold of the material.

Please replace the last full paragraph on page 11 with the following:

*AB*

Plate A exhibited steady crack growth in air at 325°C at an initial rapid rate which dropped to a slower steady state rate of  $1.5 \times 10^{-4}$  in/s approximately 175 seconds after load application. The crack propagation rate then accelerated to a rate of  $10^{-2}$  in/s as the stress intensity increased because of crack extension. Specimen failure occurred. SEM fractography showed that fracture was by ductile microvoid nucleation and growth. Similar transient high rate cracking, slower steady state cracking, and tertiary cracking behavior has been observed in creep cracking of rotor steels. The failure of Plate A in air at 325°C is thus best described as creep cracking.

Please replace the first full paragraph on page 12 with the following:

*AB*

Plate B exhibited an initial crack growth rate of  $10^{-3}$  in/s in air at 325°C at the same 32 ksi $\sqrt{\text{in}}$  stress intensity, Figures 5A and 6B. The crack propagation rate of Plate B dropped rapidly to  $10^{-7}$  in/s immediately after loading, however, and further crack advance was minimal. After 5000 seconds, the stress intensity of Plate B was increased

*Alb cont.*

to 38 ksi $\sqrt{\text{in}}$  and the resulting crack advance is shown in Figure 5B. After loading to 38 ksi $\sqrt{\text{in}}$ , the sample exhibited a transient high propagation rate followed by a slower steady state rate and then acceleration to failure at higher stress intensities. The minimum crack propagation rate of Plate B was  $5 \times 10^{-5}$  in/s which occurred at a stress intensity of 45 ksi $\sqrt{\text{in}}$ . SEM fractography showed that failure was also by ductile microvoid nucleation and growth.

*AM*

Please replace the third full paragraph on page 12 with the following:

A comparison of 325°C air and hydrogen cracking of Plate A in Figures 2A and 2B and 5A and 5B showed that the rate of cracking of Plate A in hydrogen gas at 750 psig was much faster than the rate of creep cracking in air at that stress intensity. The initial rate of cracking in both air and hydrogen were similar, but while air cracking followed a curve of decreasing crack rate, hydrogen cracking accelerated rapidly to a maximum value of 0.05 to 0.15 in/s. SEM fractography showed that the sample that was tested in air had a locally ductile micro dimpled fracture surface while the sample of Plate A that was tested in hydrogen had a perfectly brittle fracture surface.

*Alb*

Please replace the ABSTRACT with the following:

The present invention provides a creep resistant zirconium alloy comprising a coarse grained lath alpha microstructure. The microstructure can include small second phase precipitates. The small second phase precipitates can have a diameter less than 0.15 $\mu\text{m}$ . The microstructure can be partially recrystallized. The microstructure is an acicular structure and can include a lath spacing within the range from about 0.5 to about 3.0 $\mu\text{m}$ . The present invention provides a nuclear fuel cladding comprising an annular layer of the creep resistant zirconium alloy. The present invention also provides a method of manufacturing a creep resistant zirconium alloy comprising the steps of beta heat treating a zirconium alloy to form a first intermediate, fast quenching the first intermediate to form a second intermediate, cold working the second intermediate within